Leaching behaviour of hexabromocyclododecane from treated curtains

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DOI:
10.1016/j.chemosphere.2015.10.121

Document Version
Peer reviewed version

Citation for published version (Harvard):
Stubbings, WA, Kajiwara, N, Takigami, H & Harrad, S 2016, 'Leaching behaviour of hexabromocyclododecane from treated curtains', *Chemosphere*, vol. 144, pp. 2091-2096.
https://doi.org/10.1016/j.chemosphere.2015.10.121

Elsevier Editorial System(tm) for
Chemosphere

Manuscript Draft

Manuscript Number: CHEM37214R1

Title: LEACHING BEHAVIOUR OF HEXABROMOCYCLODODECANE FROM TREATED CURTAINS

Article Type: Research paper

Section/Category: Persisten Organic Pollutants and Dioxins

Keywords: Hexabromocyclododecane;
Waste soft furnishings;
Landfill;
Brominated flame retardants;
Leaching

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Corresponding Author's Institution: University of Birmingham

First Author: William Andrew Stubbings

Order of Authors: William Andrew Stubbings

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[2]Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, 305-8506, Japan.

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Abstract

A series of laboratory experiments were conducted, whereby two HBCDD treated polyester curtain samples were contacted with deionised Milli-Q water as leaching fluid and HBCDD determined in the resulting leachate. As well as single batch (no replenishment of leaching fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid at various time intervals) experiments were conducted. In single batch experiments at 20˚C, ΣHBCDD concentrations increased only slightly with increasing contact time (6 h, 24 h, and 48 h). This is supported by serial batch tests at 20 ˚C in which leaching fluid was replaced after 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Data from these experiments show that while concentrations of HBCDD in leachate after 24 h cumulative contact time exceed those at 6 h; concentrations in samples collected at subsequent contact times remained steady at ~50% of those in the 24 h sample. Consistent with this, leaching is shown to be second order, whereby a period of initially intense dissolution of more labile HBCDD is followed by a slower stage corresponding to external diffusion of the soluble residue within the textile. In experiments conducted at 20˚C, α-HBCDD is preferentially leached compared to β- and γ-HBCDD. However, at higher temperatures, the relatively more hydrophobic diastereomers are proportionally more readily leached, i.e. raising the temperature from 20°C to 80°C increased concentrations of γ-HBCDD in the leachate by a factor of 28–33 while corresponding α-HBCDD concentrations only increased by a factor of 4.3-4.8.

Keywords

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1. Introduction

Hexabromocyclododecane (HBCDD) has been identified as an endocrine disrupting chemical that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects in humans at relatively low exposure levels (Darnerud, 2003, 2008; van der Ven et al., 2006, 2009; Yamada-Okabe et al., 2005). This is compounded by evidence that its presence in the environment is ubiquitous (de Wit, 2002; Gerecke et al., 2003; Janak et al., 2005; Remberger et al., 2004; Tomy et al., 2004; Law et al., 2005, 2006; Covaci et al., 2006; de Wit et al., 2006; Marvin et al., 2006; Kohler et al., 2008; Harrad et al., 2009; Harrad et al., 2010). In a legislative context, HBCDD has been identified by the European Union as a Substance of Very High Concern, meeting the criteria of a PBT (persistent, bioaccumulative and toxic) substance (ECHA, 2014); while in Japan, HBCDD has been designated as a Monitoring Chemical Substance under the Chemical Substances Control Law because of its persistence and high bio-accumulation. Moreover, in 2013, HBCDD was listed as a persistent organic pollutant (POP) by the United Nations Environment Programme (UNEP) under the Stockholm Convention on POPs. In 2011, annual global production of HBCDD was an estimated maximum of 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in Europe and the US) (UNEP, 2011). Around 90% of HBCDD is used in the building industry, typically added at ~3% by weight into extruded or expanded polystyrene foam in rigid insulation panels/boards (EC, 2011; Marvin et al., 2011). Additionally, around 8% of HBCDD was used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered furniture and transportation seating, bed mattress ticking, draperies and wall coverings, interior textiles, e.g. roller blinds, and vehicle interior textiles. HBCDD can also be used in thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an aqueous suspension or emulsion at a loading of 8-11% by weight (EC, 2011; UNEP, 2011; Weil and Levchik, 2008). Currently, used furniture or textiles containing textiles treated with HBCDD are widely treated as municipal rather than hazardous waste, and are thus landfilled or incinerated. In the UK alone, WRAP (2012) estimated that in 2010/11 around 670,000 tonnes of furniture (an unknown fraction of which will consist of fabric coverings) and 310,000 tonnes of textiles are disposed of by householders annually. This reservoir of HBCDDs within soft furnishings has and will continue to, gradually enter the waste stream,

and there is hence a pressing need to understand the fate of chemicals like HBCDD associated with waste fabrics following disposal (Stubbings & Harrad, 2014). Potential emission pathways for chemicals associated with landfill include contamination of leachate and volatilisation. The physicochemical properties of HBCDD (water solubility = α-HBCDD (41,000 ng L^{-1}), β-HBCDD (15,000 ng L^{-1}) and γ-HBCDD (2,400 ng L^{-1}) at 20 °C, vapour pressure = 6.27 × 10^{-5} Pa at 21°C and Log K_{OW} = 5.625 (EC, 2008; Arnot et al., 2009)), suggest that following disposal to landfill such leaching and volatilisation of HBCDD associated with treated fabrics may not be extensive. However, other brominated flame retardants with similar physicochemical properties like polybrominated diphenyl ethers (PBDEs), have been reported in landfill leachate (Oliaei et al., 2002; Osako et al., 2004; Oliaei et al., 2010). In the absence to our knowledge of empirical data related to the fate of HBCDD in landfill, this study conducts a series of controlled laboratory experiments to test the hypothesis that HBCDDs are capable of leaching from waste textiles.

2. Materials and methods

2.1. Samples

We investigated two types of flame-retardant-treated polyester upholstery textiles (designated A and B) used to manufacture curtains. Each was made by a different Japanese manufacturer, with all purchased in either August or September 2007. In previous studies (Kajiwara et al.,2009; 2013; Kajwara and Takigami, 2013), it was confirmed that both textiles A and B had been treated with technical HBCDD.

2.2. Leaching test methods

Three distinct experimental scenarios were undertaken to examine the effects on the leaching behaviour of HBCDD from curtain textile material of: (a) textile-leachate contact time (single batch), (b) duration of serial or periodic wetting and draining of the textile (serial batch), and (c) leachate temperature. In single batch experiments, textile samples were contacted once only with the leaching fluid for either 6 h, 24 h or 48 h. In contrast, in serial batch experiments, textiles were contacted with the leaching fluid for 168 h in total,

with leachate removed from the contact vessel and replenished with fresh leaching fluid at intervals of 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Finally, to examine the influence of the temperature of the leaching fluid on leaching behaviour, single batch experiments were conducted in which textiles were contacted with leaching fluid for 24 h at three different temperatures (20, 50, and 80 °C). Fresh textile samples were used for each temperature. The concentration of HBCDD was measured in each leachate sample generated. Conditions employed in these experiments are summarised in Supplementary Information. All experiments were conducted in PTFE bottles (500 mL). Curtain textile samples were first cut into 5 x 5 cm squares and 10 grams weighed accurately before addition to the PTFE contact vessel. In all experiments, the leaching fluid used was 250 mL of Milli-Q purified, deionised water giving a liquid-solid ratio of 25:1 (v/w). Following addition of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time. The exception was for experiments examining the influence of temperature (20, 50, and 80 °C), which were not agitated and instead were maintained at the desired temperature for 24 h by immersion of the contact vessel in a thermostatically controlled water bath. Each experiment was conducted in duplicate.

2.3. Sample preparation and chemical analysis

Each leachate sample was filtered through a 0.50 µm size particle retention glass fibre filter (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with 60 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs as internal (or surrogate) standards. The filtrate was then extracted in series using 2 x 50 mL dichloromethane (DCM) by liquid-liquid extraction with mechanical shaking for 30 minutes each time. Approximately 5-10 mL 2% NaCl solution was used to enhance separation after extraction. The combined DCM extracts were dried via filtration through Na_2SO_4. The dried extract was concentrated with solvent exchange to hexane before elution through a pre-cleaned acidified silica (1 g of 22% concentrated sulfuric acid, w/w) and Na_2SO_4 column with 30 mL of n-hexane/DCM 9:1 (v/v). The eluate was concentrated with solvent exchange to hexane before evaporation to incipient dryness, addition of d_{18}-labelled α-, β-, and γ-HBCDD as recovery (or syringe) standard and dilution in methanol prior to analysis via LC-ESI-MS/MS.

Concentrations of HBCDDs in test fabrics were determined in accordance with Kajiwara et al. (2009). Briefly, a textile sample (~0.2 g) was added to 20 mL of DCM in a glass bottle with a lid; the bottle was shaken by hand for 2 minutes and then kept in the dark at room temperature for 2 days. A 200 µL aliquot of the crude extract obtained by this method was diluted with 20 mL toluene. A 50 µL aliquot of the toluene was spiked with 50 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs as internal standards prior to further dilution to 1 mL with methanol. Each test fabric was analysed in triplicate.

2.4 Determination of concentrations of HBCDDs

For samples generated in single and serial batch experiments, HBCDDs were quantified using an Alliance 2695 liquid chromatograph equipped with a Quattro Ultima triple quadrupole mass spectrometer (Waters, Tokyo, Japan) (see supporting information for additional details). Concentrations of HBCDDs in samples generated in experiments examining the impact on leaching of variable leaching fluid temperature, were quantified using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) (see supporting information for additional details).

2.5. Calculation of HBCDD leaching

The percentage of HBCDDs present in the test textiles that was leached into each leachate samples (PL) was calculated as follows (equation 1):

Equation 1: $PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W}\right] \times 100\%$

PL = percentage leached (%)

$C_{leachate}$ = Conc. of HBCDD collected in leachate (mg/L)

V = volume of leachate (L)

170 C_{waste} = Conc. of HBCDD in waste sample (mg/kg)

171 W = total weight of waste sample (kg)

172 The percentage leached normalised to contact time (*PLT*, % h^{-1}) is expressed here as the
173 percentage of HBCDD leached from the textile per hour of contact time. *PLT* is calculated
174 according to equation 2.

175 Equation 2: $PLT = \frac{PL}{t}$

176 *PL* = percentage leached (%)

177 *t* = contact time (h)

178

179 **3. Results and discussion**

180 **3.1. Initial HBCDD concentrations and diastereomer profiles in the textile samples**

181 Table 1 displays the initial concentrations of HBCDD and individual diastereomers in the
182 treated textile samples used in this study. The textiles were analysed for α-, β-, γ-, δ- and ε-
183 HBCDD diastereomers. HBCDD is prepared commercially by bromination of *cis,trans,trans*-
184 cyclododecatriene (ctt-CDT) while δ- and ε- are formed by bromination of *trans,trans,trans*-
185 cyclododecatriene (ttt-CDT), a common contaminant in commercial ctt-CDT (Arsenault et al.,
186 2007). However, while traces of δ- and ε- were detected in our textile samples, their
187 concentrations were below the limit of quantitation (<500 mg kg^{-1} and <300 mg kg^{-1}
188 respectively).

189 Depending on the manufacturer and the production method used, technical grade HBCDD
190 consists of 75-95 % γ-HBCDD, 3-13 % α- HBCDD and 0.5-12 % β-HBCDD (Becher, 2005; UNEP,
191 2011). In contrast, the HBCDD diastereomer pattern in the textiles used in this study was
192 roughly equally distributed between α- and γ- with a smaller proportion of β-HBCDD. The
193 difference between the diastereomer pattern observed in these samples and that reported
194 for technical grade HBCDD is likely due to the processes via which the textiles are flame-
195 retarded. HBCDD is applied via immersion of the textiles in a solution of technical HBCDD.
196 Following removal of the textile from the solution, the textile is desiccated at ~100-190 °C

(Johokiko, 2008). Thermal isomerisation of HBCDD towards a composition relatively enriched in α-HBCD compared to the starting material has been demonstrated previously (Köppen et al, 2008) and appears a plausible explanation for the pattern observed in our textile samples.

3.2. Effects of contact time on leaching (single batch experiments)

The influence of contact time on HBCDD concentrations in leachate in single batch experiments conducted at 20 ˚C is illustrated by Figure 1, with leaching behaviour for the same experiments provided in the Supplementary Information. Only a slight increase in HBCDD concentrations detected in leachate was observed on increasing contact time from 6 to 24 and then 48 h. As a consequence, *PLT* decreases with increasing contact time. This suggests the majority of HBCDD leaching occurs in the first six hours of contact between the fabric source and the leaching fluid, thereafter, *PLT* diminishes. Moreover, in all experiments conducted at 20 ˚C, α-HBCDD leached far more extensively than β-HBCDD or γ-HBCDD. We believe that these diastereomer-specific variations in *PLT* are explicable in terms of the aqueous solubility of HBCDD. Specifically, the aqueous solubility of α-HBCDD (41 μg L^{-1}), exceeds that of both β-HBCDD (15 μg L^{-1}) and γ-HBCDD (2.4 μg L^{-1}) at 20 °C (EC, 2008; Arnot et al., 2009).

Intriguingly, while ε-HBCDD was below the limit of quantitation in the curtain textile samples (Table 1), it was detected in the leachate in both single (Figure 1) and serial batch experiments (Figures 2 & 3). This suggests either that ε-HBCDD is present in the textile (but below detection limit) and is substantially more water soluble than other HBCDD diastereomers, and thus leached more efficiently; or that it is formed as a result of isomerisation processes (Heeb et al, 2008; Köppen et al, 2008).

3.3. Effect of cyclical wetting and draining on HBCDD concentrations and leaching behaviour (serial batch experiments).

Concentrations of HBCDDs (ng L^{-1}) detected in leachate and *PLT* values (% h^{-1}) obtained from these experiments on both textiles A and B are presented in Figures 2 and 3. After 24 h cumulative contact time, concentrations of HBCDD leached from both textiles in these serial batch experiments diminish with increasing experimental duration. However, the decline in concentration is not dramatic, and even after a cumulative 168 h of leaching, the ΣHBCDD concentration >50% of that observed after just 6 h leaching. The observed decline in leachate concentration with successive batches may be attributable to removal in the early contact periods of less tightly bound HBCDD present on the surface of the textile. Overall – although longer term experiments are required to confirm this - this serial batch experiment indicates that replenishment of leaching fluid as would be expected in a landfill does not result in diminished HBCDD leaching from textiles over long periods. Unfortunately, insufficient material was available to us to conduct these longer term tests.

3.4. Leaching kinetics

Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in terms of the following second-order rate equation:

Equation 3: $$\frac{Ct}{t} = k(Cs - Ct)^2 ,$$

where *k* is the second-order leaching rate constant (L ng^{-1} min^{-1}), *Cs* the leaching capacity, which is the concentration of HBCDD at saturation (ng L^{-1}), and *Ct* is the concentration of HBCDD (ng L^{-1}) in suspension at any given time, *t* (min). The leaching capacity, *Cs*, and the second-order leaching rate constant, *k*, can be determined experimentally from the slope and intercept by plotting *t*/*Ct* against *t*.

We generated such plots for all our experiments conducted at 20 ˚C. We combined data at that temperature for both single batch and serial batch experiments, by treating our serial batch experiments as a series of single batch experiments. A positive and highly significant linear correlation between t/C_t and t was observed in all instances. Plots are provided for Textile A and B in Supplementary Information. This apparent fit with second order kinetics confirms our observations above of initial rapid leaching followed by a slower second phase.

We suggest that initially there is intense dissolution in which maximum leaching takes place as a result of removal from the fabric of HBCDD that is more loosely associated with easily abraded fibres and present on the fabric surface rather than embedded within the fabric. A second, slower stage follows, which corresponds primarily to external diffusion and is related to the soluble remainder. The slope, Y-intercept, saturated leaching capacity, *Cs*, the leaching rate constant, *k*, two-tailed *p* values, and Pearson's correlation coefficients, *r*, are given for individual HBCDD diastereomers in Table 2.

3.5. Effect of temperature on leaching

Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on *PLT* of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated.

Concentrations and leaching behaviour of HBCDD from textiles A and B at different temperatures are displayed in Figures 4 & 5, with the diastereomer pattern in leachate at different temperatures shown in Supplementary Information. Note that while ε-HBCDD was detected in leachate at 20 ˚C experiments (section 3.3), it was not found at quantifiable levels in experiments run at higher temperatures. This suggests thermal instability of ε-HBCDD. While concentrations of all diastereomers increased with increasing temperature, raising the temperature from 20 °C to 80 °C increased leachate concentrations of γ-HBCDD by a factor of 28 - 33, while α-HBCDD concentrations only increased by a factor of 4.3 - 4.8. One possible explanation for this observation is that at higher temperatures the relatively more hydrophobic isomers (β-HBCDD and γ-HBCDD) become more water soluble compared to α-HBCDD and are therefore more readily leached. Alternatively, isomerisation may occur at lower temperatures than hitherto documented.

3.6. Effect of agitation on leaching

By comparing the results of experiments conducted at 20 °C with contact times of 24 h in the agitation time experiment and the temperature experiment the effect of agitation on leaching of HBCDD from the textiles can be examined. The ΣHBCDD concentrations in the agitated leachate samples were 36 times higher for Textile A and 20 times higher for Textile

B. This illustrates that agitation has a considerable role in enhancing HBCDD leachate concentrations from treated textiles.

4. Summary

This study demonstrates that leaching of HBCDD from textiles using distilled deionised water as a leaching fluid is a second order process. Following an initial period of source:leaching fluid contact during which leaching is relatively facile, subsequent leaching is slower. Leaching is higher for the more water soluble diastereomers and is substantially greater at 80 ˚C compared to 20 ˚C. Our data, when combined with the plausibly enhanced solubility of BFRs in leaching fluid containing dissolved organic matter (Choi et al, 2009), and existing reports of measurable concentrations of HBCDD in landfill leachate (Morris et al., 2004; Remberger et al., 2004; Suzuki and Hasegawa, 2006), suggests that leaching of HBCDD from landfilled waste requires further study to elucidate its magnitude, the factors influencing it, and its environmental impact.

Acknowledgements

The authors acknowledge gratefully the provision of an Open Competition CASE studentship award to WAS by the UK Natural Environment Research Council (NERC ref NE/I018352/1). Additional financial support to WAS from Ricardo-AEA is also acknowledged gratefully. The research leading to these results has received funding from the European Union Seventh Framework Programme (*FP7/2007-2013*) under grant agreement 295138 (INTERFLAME).

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468 **Table 1: Mean Concentrations (mg kg^{-1}) of HBCDDs in textiles used in this study**

Diastereomer/ Sample	α-HBCDD	β-HBCDD	γ-HBCDD	δ-HBCDD	ε-HBCDD	ΣHBCDD
Textile A	11,000 ± 55	4,500 ± 130	10,000 ± 160	<500	<300	26,000 ± 170
Textile B	9,900 ± 200	3,600 ± 100	10,000 ± 130	<500	<300	24,000 ± 420

Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

469

470

471 **Table 2: Second order leaching rate constants (*k*) and saturated leaching capacities (C_s)**
472 **obtained for HBCDD diastereomers for Textiles A and B[a]**

Constant / Compound	Slope	y-intercept	C_s (ng L^{-1})	Observed max. conc. (ng L^{-1})	*k* (L ng^{-1} min^{-1})	*Two-tailed P value*	*Correlation coefficient: r*
Textile A							
β-HBCDD	0.0056	0.9249	180	220	0.000012	.000	0.945
γ-HBCDD	0.0043	1.1723	230	410	0.000007	.000	0.832
Textile B							
γ-HBCDD	0.0082	3.5252	120	380	0.000019	.000	0.896

[a]Data not shown for plots for which y-intercept and thus *k* values were negative.

473

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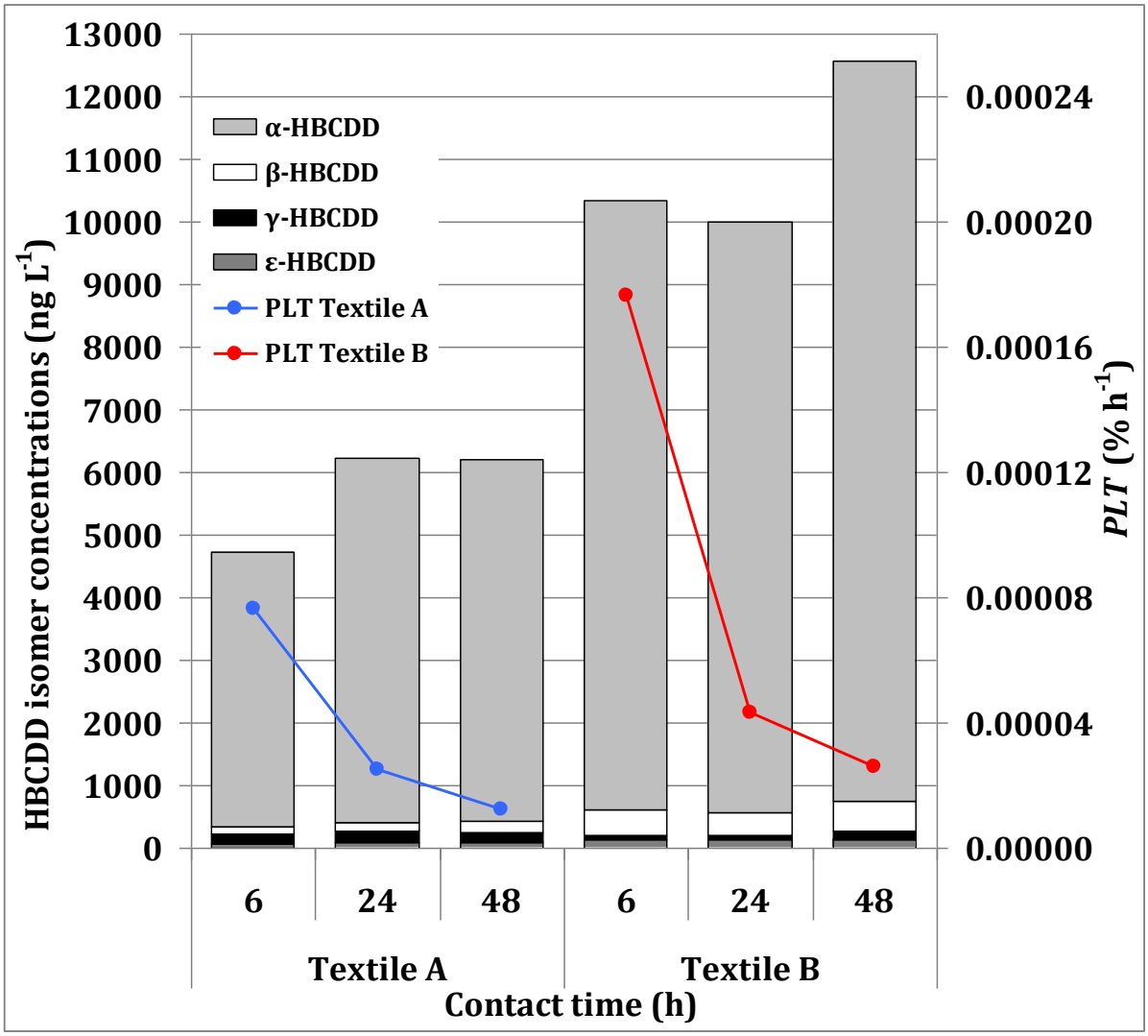
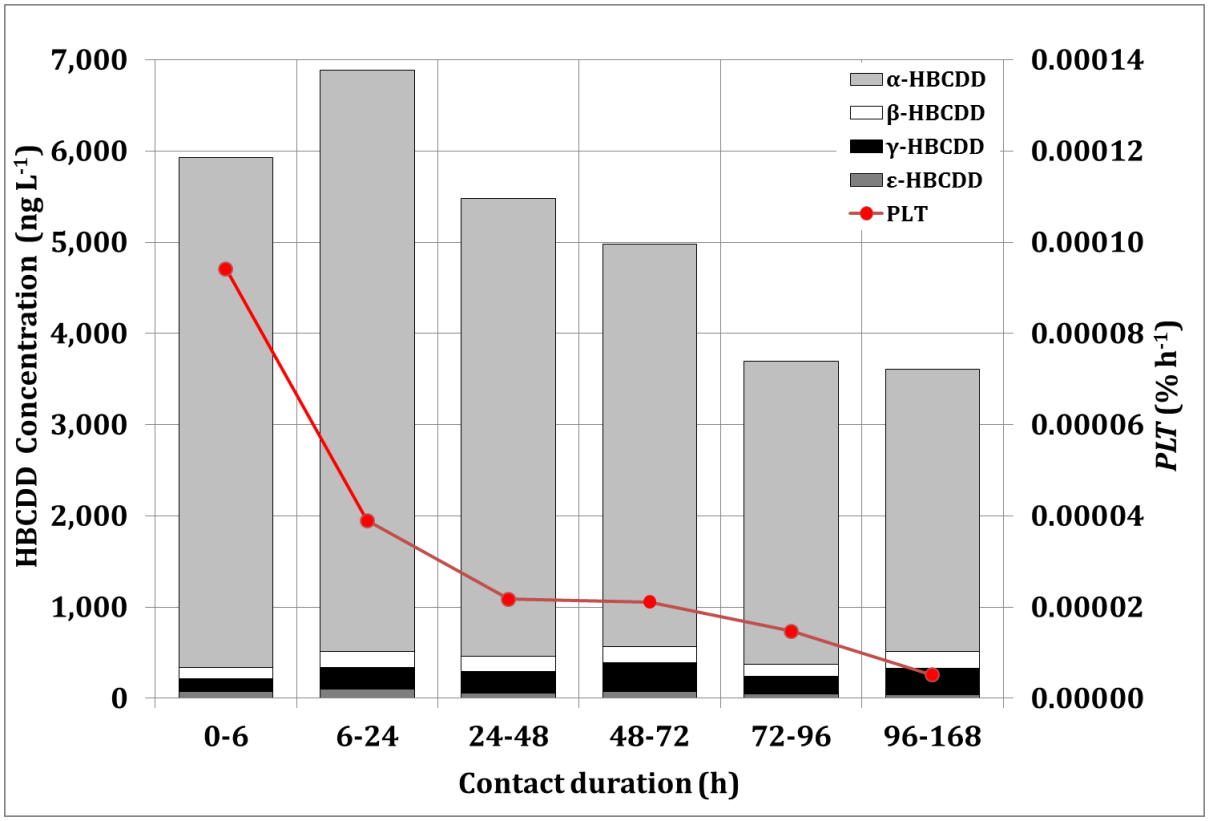


476

477 **Fig. 1: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate**
478 **produced from single batch experiments on Textiles A & B for different agitation times.**

479



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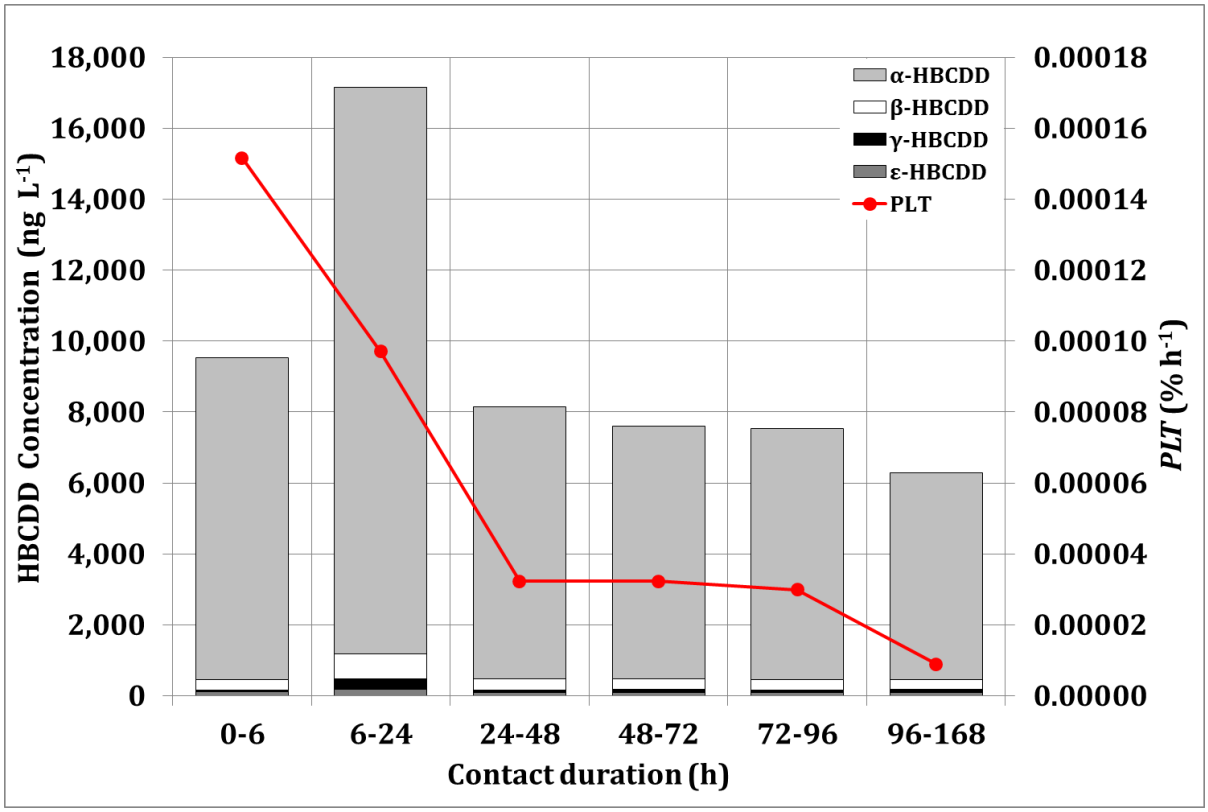
481 **Fig. 2 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate**
482 **produced during serial batch experiments on Textile A examining the effect of cyclical**
483 **wetting and draining.**

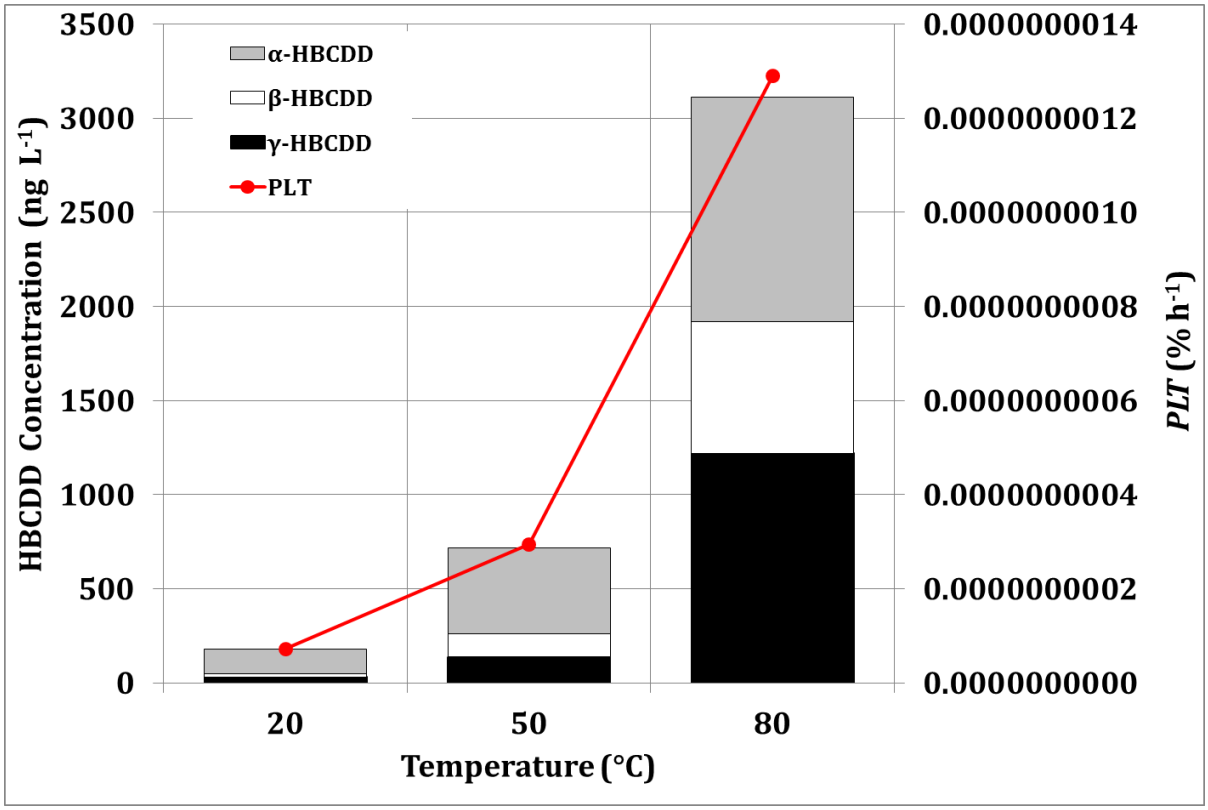
484



485

486 **Fig. 3 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate**
487 **produced during serial batch experiments on Textile B examining the effect of cyclical**
488 **wetting and draining.**

489



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491 **Fig. 4 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) from Textile A at**
492 **different temperatures during 24h single batch experiments.**

493

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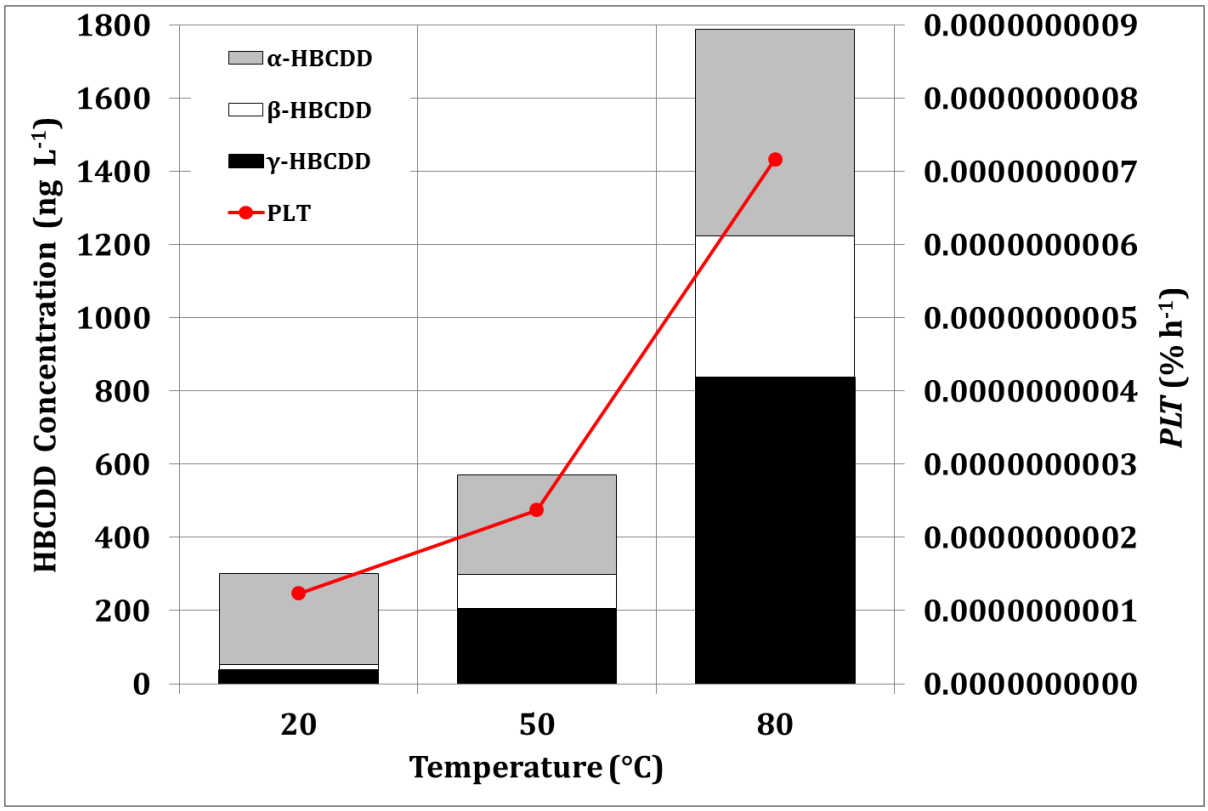

495

496 **Fig. 5 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) from Textile B at**
497 **different temperatures during 24h single batch experiments.**

498

Highlights

- We study HBCDD leaching from contacting a treated textile with deionised water
- Leaching of HBCDD from textiles is shown to be a second order process
- α-HBCDD is preferentially leached compared to β- and γ-HBCDD at 20 °C
- At 80 °C γ-HBCDD is proportionally more readily leached than α-HBCDD
- While not detected in the textile, ε-HBCDD was detected in leachate
- A max. total HBCDD conc. of 20,000 ng L^{-1} was detected in the leachate

LEACHING BEHAVIOUR OF HEXABROMOCYCLODODECANE FROM TREATED CURTAINS

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Abstract

A series of laboratory experiments were conducted, whereby two HBCDD treated polyester curtain samples were contacted with deionised Milli-Q water as leaching fluid and HBCDD determined in the resulting leachate. As well as single batch (no replenishment of leaching fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid at various time intervals) experiments were conducted. In single batch experiments at 20˚C, ΣHBCDD concentrations increased only slightly with increasing contact time (6 h, 24 h, and 48 h). This is supported by serial batch tests at 20 ˚C in which leaching fluid was replaced after 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Data from these experiments show that while concentrations of HBCDD in leachate after 24 h cumulative contact time exceed those at 6 h; concentrations in samples collected at subsequent contact times remained steady at ~50% of those in the 24 h sample. Consistent with this, leaching is shown to be second order, whereby a period of initially intense dissolution of more labile HBCDD is followed by a slower stage corresponding to external diffusion of the soluble residue within the textile. In experiments conducted at 20˚C, α-HBCDD is preferentially leached compared to β- and γ-HBCDD. However, at higher temperatures, the relatively more hydrophobic diastereomers are proportionally more readily leached, i.e. raising the temperature from 20°C to 80°C increased concentrations of γ-HBCDD in the leachate by a factor of 28–33 while corresponding α-HBCDD concentrations only increased by a factor of 4.3-4.8.

Keywords

Hexabromocyclododecane;

Waste soft furnishings;

Landfill;

Brominated flame retardants;

Leaching

1. Introduction

Hexabromocyclododecane (HBCDD) has been identified as an endocrine disrupting chemical that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects in humans at relatively low exposure levels (Darnerud, 2003, 2008; van der Ven et al., 2006, 2009; Yamada-Okabe et al., 2005). This is compounded by evidence that its presence in the environment is ubiquitous (de Wit, 2002; Gerecke et al., 2003; Janak et al., 2005; Remberger et al., 2004; Tomy et al., 2004; Law et al., 2005, 2006; Covaci et al., 2006; de Wit et al., 2006; Marvin et al., 2006; Kohler et al., 2008; Harrad et al., 2009; Harrad et al., 2010). In a legislative context, HBCDD has been identified by the European Union as a Substance of Very High Concern, meeting the criteria of a PBT (persistent, bioaccumulative and toxic) substance (ECHA, 2014); while in Japan, HBCDD has been designated as a Monitoring Chemical Substance under the Chemical Substances Control Law because of its persistence and high bio-accumulation. Moreover, in 2013, HBCDD was listed as a persistent organic pollutant (POP) by the United Nations Environment Programme (UNEP) under the Stockholm Convention on POPs. In 2011, annual global production of HBCDD was an estimated maximum of 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in Europe and the US) (UNEP, 2011). Around 90% of HBCDD is used in the building industry, typically added at ~3% by weight into extruded or expanded polystyrene foam in rigid insulation panels/boards (EC, 2011; Marvin et al., 2011). Additionally, around 8% of HBCDD was used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered furniture and transportation seating, bed mattress ticking, draperies and wall coverings, interior textiles, e.g. roller blinds, and vehicle interior textiles. HBCDD can also be used in thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an aqueous suspension or emulsion at a loading of 8-11% by weight (EC, 2011; UNEP, 2011; Weil and Levchik, 2008). Currently, used furniture or textiles containing textiles treated with HBCDD are widely treated as municipal rather than hazardous waste, and are thus landfilled or incinerated. In the UK alone, WRAP (2012) estimated that in 2010/11 around 670,000 tonnes of furniture (an unknown fraction of which will consist of fabric coverings) and 310,000 tonnes of textiles are disposed of by householders annually. This reservoir of HBCDDs within soft furnishings has and will continue to, gradually enter the waste stream,

and there is hence a pressing need to understand the fate of chemicals like HBCDD associated with waste fabrics following disposal (Stubbings & Harrad, 2014). Potential emission pathways for chemicals associated with landfill include contamination of leachate and volatilisation. The physicochemical properties of HBCDD (water solubility = α-HBCDD (41,000 ng L^{-1}), β-HBCDD (15,000 ng L^{-1}) and γ-HBCDD (2,400 ng L^{-1}) at 20 °C, vapour pressure = 6.27×10^{-5} Pa at 21°C and Log K_{OW} = 5.625 (EC, 2008; Arnot et al., 2009)), suggest that following disposal to landfill such leaching and volatilisation of HBCDD associated with treated fabrics may not be extensive. However, other brominated flame retardants with similar physicochemical properties like polybrominated diphenyl ethers (PBDEs), have been reported in landfill leachate (Oliaei et al., 2002; Osako et al., 2004; Oliaei et al., 2010). In the absence to our knowledge of empirical data related to the fate of HBCDD in landfill, this study conducts a series of controlled laboratory experiments to test the hypothesis that HBCDDs are capable of leaching from waste textiles.

2. Materials and methods

2.1. Samples

We investigated two types of flame-retardant-treated polyester upholstery textiles (designated A and B) used to manufacture curtains. Each was made by a different Japanese manufacturer, with all purchased in either August or September 2007. In previous studies (Kajiwara et al.,2009; 2013; Kajwara and Takigami, 2013), it was confirmed that both textiles A and B had been treated with technical HBCDD.

2.2. Leaching test methods

Three distinct experimental scenarios were undertaken to examine the effects on the leaching behaviour of HBCDD from curtain textile material of: (a) textile-leachate contact time (single batch), (b) duration of serial or periodic wetting and draining of the textile (serial batch), and (c) leachate temperature. In single batch experiments, textile samples were contacted once only with the leaching fluid for either 6 h, 24 h or 48 h. In contrast, in serial batch experiments, textiles were contacted with the leaching fluid for 168 h in total,

with leachate removed from the contact vessel and replenished with fresh leaching fluid at intervals of 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Finally, to examine the influence of the temperature of the leaching fluid on leaching behaviour, single batch experiments were conducted in which textiles were contacted with leaching fluid for 24 h at three different temperatures (20, 50, and 80 °C). Fresh textile samples were used for each temperature. The concentration of HBCDD was measured in each leachate sample generated. Conditions employed in these experiments are summarised in Supplementary Information. All experiments were conducted in PTFE bottles (500 mL). Curtain textile samples were first cut into 5 x 5 cm squares and 10 grams weighed accurately before addition to the PTFE contact vessel. In all experiments, the leaching fluid used was 250 mL of Milli-Q purified, deionised water giving a liquid-solid ratio of 25:1 (v/w). Following addition of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time. The exception was for experiments examining the influence of temperature (20, 50, and 80 °C), which were not agitated and instead were maintained at the desired temperature for 24 h by immersion of the contact vessel in a thermostatically controlled water bath. Each experiment was conducted in duplicate.

2.3. Sample preparation and chemical analysis

Each leachate sample was filtered through a 0.50 µm size particle retention glass fibre filter (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with 60 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs as internal (or surrogate) standards. The filtrate was then extracted in series using 2 x 50 mL dichloromethane (DCM) by liquid-liquid extraction with mechanical shaking for 30 minutes each time. Approximately 5-10 mL 2% NaCl solution was used to enhance separation after extraction. The combined DCM extracts were dried via filtration through Na_2SO_4. The dried extract was concentrated with solvent exchange to hexane before elution through a pre-cleaned acidified silica (1 g of 22% concentrated sulfuric acid, w/w) and Na_2SO_4 column with 30 mL of n-hexane/DCM 9:1 (v/v). The eluate was concentrated with solvent exchange to hexane before evaporation to incipient dryness, addition of d_{18}-labelled α-, β-, and γ-HBCDD as recovery (or syringe) standard and dilution in methanol prior to analysis via LC-ESI-MS/MS.

Concentrations of HBCDDs in test fabrics were determined in accordance with Kajiwara et al. (2009). Briefly, a textile sample (~0.2 g) was added to 20 mL of DCM in a glass bottle with a lid; the bottle was shaken by hand for 2 minutes and then kept in the dark at room temperature for 2 days. A 200 µL aliquot of the crude extract obtained by this method was diluted with 20 mL toluene. A 50 µL aliquot of the toluene was spiked with 50 ng each of $^{13}C_{12}$-labelled α-, β-, and γ-HBCDDs as internal standards prior to further dilution to 1 mL with methanol. Each test fabric was analysed in triplicate.

2.4 Determination of concentrations of HBCDDs

For samples generated in single and serial batch experiments, HBCDDs were quantified using an Alliance 2695 liquid chromatograph equipped with a Quattro Ultima triple quadrupole mass spectrometer (Waters, Tokyo, Japan) (see supporting information for additional details). Concentrations of HBCDDs in samples generated in experiments examining the impact on leaching of variable leaching fluid temperature, were quantified using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) (see supporting information for additional details).

2.5. Calculation of HBCDD leaching

The percentage of HBCDDs present in the test textiles that was leached into each leachate samples (PL) was calculated as follows (equation 1):

Equation 1: $PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W}\right] \times 100\%$

PL = percentage leached (%)

$C_{leachate}$ = Conc. of HBCDD collected in leachate (mg/L)

V = volume of leachate (L)

170 C_{waste} = Conc. of HBCDD in waste sample (mg/kg)

171 W = total weight of waste sample (kg)

172 The percentage leached normalised to contact time (*PLT*, % h^{-1}) is expressed here as the
173 percentage of HBCDD leached from the textile per hour of contact time. *PLT* is calculated
174 according to equation 2.

175 Equation 2: $PLT = \frac{PL}{t}$

176 *PL* = percentage leached (%)

177 *t* = contact time (h)

178

179 **3. Results and discussion**

180 **3.1. Initial HBCDD concentrations and diastereomer profiles in the textile samples**

181 Table 1 displays the initial concentrations of HBCDD and individual diastereomers in the
182 treated textile samples used in this study. The textiles were analysed for α-, β-, γ-, δ- and ε-
183 HBCDD diastereomers. HBCDD is prepared commercially by bromination of *cis,trans,trans*-
184 cyclododecatriene (ctt-CDT) while δ- and ε- are formed by bromination of *trans,trans,trans*-
185 cyclododecatriene (ttt-CDT), a common contaminant in commercial ctt-CDT (Arsenault et al.,
186 2007). However, while traces of δ- and ε- were detected in our textile samples, their
187 concentrations were below the limit of quantitation (<500 mg kg^{-1} and <300 mg kg^{-1}
188 respectively).

189 Depending on the manufacturer and the production method used, technical grade HBCDD
190 consists of 75-95 % γ-HBCDD, 3-13 % α- HBCDD and 0.5-12 % β-HBCDD (Becher, 2005; UNEP,
191 2011). In contrast, the HBCDD diastereomer pattern in the textiles used in this study was
192 roughly equally distributed between α- and γ- with a smaller proportion of β-HBCDD. The
193 difference between the diastereomer pattern observed in these samples and that reported
194 for technical grade HBCDD is likely due to the processes via which the textiles are flame-
195 retarded. HBCDD is applied via immersion of the textiles in a solution of technical HBCDD.
196 Following removal of the textile from the solution, the textile is desiccated at ~100-190 °C

(Johokiko, 2008). Thermal isomerisation of HBCDD towards a composition relatively enriched in α-HBCD compared to the starting material has been demonstrated previously (Köppen et al, 2008) and appears a plausible explanation for the pattern observed in our textile samples.

3.2. Effects of contact time on leaching (single batch experiments)

The influence of contact time on HBCDD concentrations in leachate in single batch experiments conducted at 20 ˚C is illustrated by Figure 1, with leaching behaviour for the same experiments provided in the Supplementary Information. Only a slight increase in HBCDD concentrations detected in leachate was observed on increasing contact time from 6 to 24 and then 48 h. As a consequence, *PLT* decreases with increasing contact time. This suggests the majority of HBCDD leaching occurs in the first six hours of contact between the fabric source and the leaching fluid, thereafter, *PLT* diminishes. Moreover, in all experiments conducted at 20 ˚C, α-HBCDD leached far more extensively than β-HBCDD or γ-HBCDD. We believe that these diastereomer-specific variations in *PLT* are explicable in terms of the aqueous solubility of HBCDD. Specifically, the aqueous solubility of α-HBCDD (41 μg L^{-1}), exceeds that of both β-HBCDD (15 μg L^{-1}) and γ-HBCDD (2.4 μg L^{-1}) at 20 °C (EC, 2008; Arnot et al., 2009).

Intriguingly, while ε-HBCDD was below the limit of quantitation in the curtain textile samples (Table 1), it was detected in the leachate in both single (Figure 1) and serial batch experiments (Figures 2 & 3). This suggests either that ε-HBCDD is present in the textile (but below detection limit) and is substantially more water soluble than other HBCDD diastereomers, and thus leached more efficiently; or that it is formed as a result of isomerisation processes (Heeb et al, 2008; Köppen et al, 2008).

3.3. Effect of cyclical wetting and draining on HBCDD concentrations and leaching behaviour (serial batch experiments).

225 Concentrations of HBCDDs (ng L^{-1}) detected in leachate and *PLT* values (% h^{-1}) obtained from
226 these experiments on both textiles A and B are presented in Figures 2 and 3. After 24 h
227 cumulative contact time, concentrations of HBCDD leached from both textiles in these serial
228 batch experiments diminish with increasing experimental duration. However, the decline in
229 concentration is not dramatic, and even after a cumulative 168 h of leaching, the ΣHBCDD
230 concentration >50% of that observed after just 6 h leaching. The observed decline in
231 leachate concentration with successive batches may be attributable to removal in the early
232 contact periods of less tightly bound HBCDD present on the surface of the textile. Overall –
233 although longer term experiments are required to confirm this - this serial batch experiment
234 indicates that replenishment of leaching fluid as would be expected in a landfill does not
235 result in diminished HBCDD leaching from textiles over long periods. Unfortunately,
236 insufficient material was available to us to conduct these longer term tests.

237

238 **3.4. Leaching kinetics**

239 Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in
240 terms of the following second-order rate equation:

241 Equation 3: $$\frac{Ct}{t} = k(Cs - Ct)^2 ,$$

242 where *k* is the second-order leaching rate constant (L ng^{-1} min^{-1}), *Cs* the leaching capacity,
243 which is the concentration of HBCDD at saturation (ng L^{-1}), and *Ct* is the concentration of
244 HBCDD (ng L^{-1}) in suspension at any given time, *t* (min). The leaching capacity, *Cs*, and the
245 second-order leaching rate constant, *k*, can be determined experimentally from the slope
246 and intercept by plotting *t*/*Ct* against *t*.

247 We generated such plots for all our experiments conducted at 20 ˚C. We combined data at
248 that temperature for both single batch and serial batch experiments, by treating our serial
249 batch experiments as a series of single batch experiments. A positive and highly significant
250 linear correlation between t/C_t and t was observed in all instances. Plots are provided for
251 Textile A and B in Supplementary Information. This apparent fit with second order kinetics
252 confirms our observations above of initial rapid leaching followed by a slower second phase.

We suggest that initially there is intense dissolution in which maximum leaching takes place as a result of removal from the fabric of HBCDD that is more loosely associated with easily abraded fibres and present on the fabric surface rather than embedded within the fabric. A second, slower stage follows, which corresponds primarily to external diffusion and is related to the soluble remainder. The slope, Y-intercept, saturated leaching capacity, *Cs*, the leaching rate constant, *k*, two-tailed *p* values, and Pearson's correlation coefficients, *r*, are given for individual HBCDD diastereomers in Table 2.

3.5. Effect of temperature on leaching

Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on *PLT* of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated.

Concentrations and leaching behaviour of HBCDD from textiles A and B at different temperatures are displayed in Figures 4 & 5, with the diastereomer pattern in leachate at different temperatures shown in Supplementary Information. Note that while ε-HBCDD was detected in leachate at 20 ˚C experiments (section 3.3), it was not found at quantifiable levels in experiments run at higher temperatures. This suggests thermal instability of ε-HBCDD. While concentrations of all diastereomers increased with increasing temperature, raising the temperature from 20 °C to 80 °C increased leachate concentrations of γ-HBCDD by a factor of 28 - 33, while α-HBCDD concentrations only increased by a factor of 4.3 - 4.8. One possible explanation for this observation is that at higher temperatures the relatively more hydrophobic isomers (β-HBCDD and γ-HBCDD) become more water soluble compared to α-HBCDD and are therefore more readily leached. Alternatively, isomerisation may occur at lower temperatures than hitherto documented.

3.6. Effect of agitation on leaching

By comparing the results of experiments conducted at 20 °C with contact times of 24 h in the agitation time experiment and the temperature experiment the effect of agitation on leaching of HBCDD from the textiles can be examined. The ΣHBCDD concentrations in the agitated leachate samples were 36 times higher for Textile A and 20 times higher for Textile

B. This illustrates that agitation has a considerable role in enhancing HBCDD leachate concentrations from treated textiles.

4. Summary

This study demonstrates that leaching of HBCDD from textiles using distilled deionised water as a leaching fluid is a second order process. Following an initial period of source:leaching fluid contact during which leaching is relatively facile, subsequent leaching is slower. Leaching is higher for the more water soluble diastereomers and is substantially greater at 80 ˚C compared to 20 ˚C. Our data, when combined with the plausibly enhanced solubility of BFRs in leaching fluid containing dissolved organic matter (Choi et al, 2009), and existing reports of measurable concentrations of HBCDD in landfill leachate (Morris et al., 2004; Remberger et al., 2004; Suzuki and Hasegawa, 2006), suggests that leaching of HBCDD from landfilled waste requires further study to elucidate its magnitude, the factors influencing it, and its environmental impact.

Acknowledgements

The authors acknowledge gratefully the provision of an Open Competition CASE studentship award to WAS by the UK Natural Environment Research Council (NERC ref NE/I018352/1). Additional financial support to WAS from Ricardo-AEA is also acknowledged gratefully. The research leading to these results has received funding from the European Union Seventh Framework Programme (*FP7/2007-2013*) under grant agreement 295138 (INTERFLAME).

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468 **Table 1: Mean Concentrations (mg kg^{-1}) of HBCDDs in textiles used in this study**

Diastereomer/ Sample	α-HBCDD	β-HBCDD	γ-HBCDD	δ-HBCDD	ε-HBCDD	ΣHBCDD
Textile A	11,000 ± 55	4,500 ± 130	10,000 ± 160	<500	<300	26,000 ± 170
Textile B	9,900 ± 200	3,600 ± 100	10,000 ± 130	<500	<300	24,000 ± 420

Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

469

470

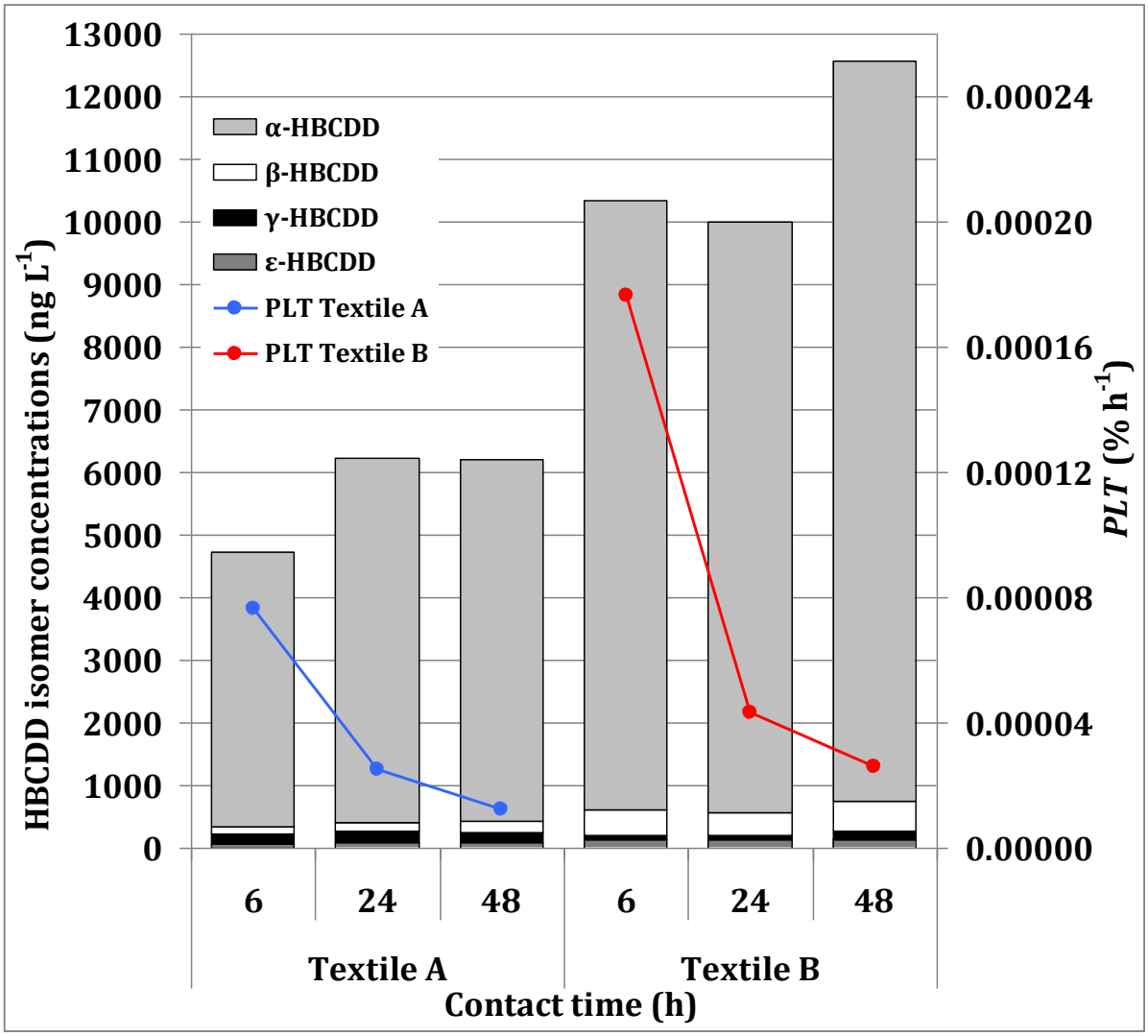
471 **Table 2: Second order leaching rate constants (*k*) and saturated leaching capacities (C_s)**
472 **obtained for HBCDD diastereomers for Textiles A and B[a]**

Constant / Compound	Slope	y-intercept	C_s (ng L^{-1})	Observed max. conc. (ng L^{-1})	*k* (L ng^{-1} min^{-1})	*Two-tailed P value*	*Correlation coefficient: r*
Textile A							
β-HBCDD	0.0056	0.9249	180	220	0.000012	.000	0.945
γ-HBCDD	0.0043	1.1723	230	410	0.000007	.000	0.832
Textile B							
γ-HBCDD	0.0082	3.5252	120	380	0.000019	.000	0.896

[a]Data not shown for plots for which y-intercept and thus *k* values were negative.

473

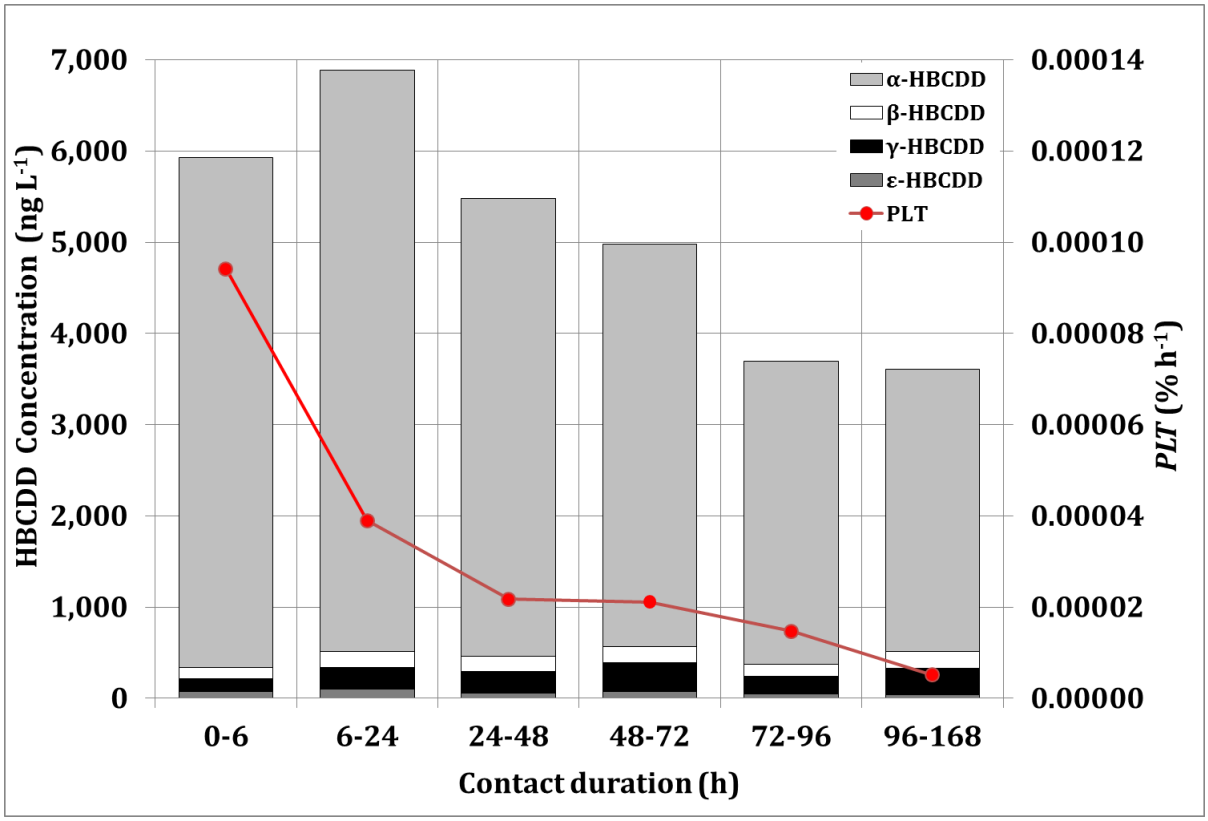
474



476

477 **Fig. 1: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate**
478 **produced from single batch experiments on Textiles A & B for different agitation times.**

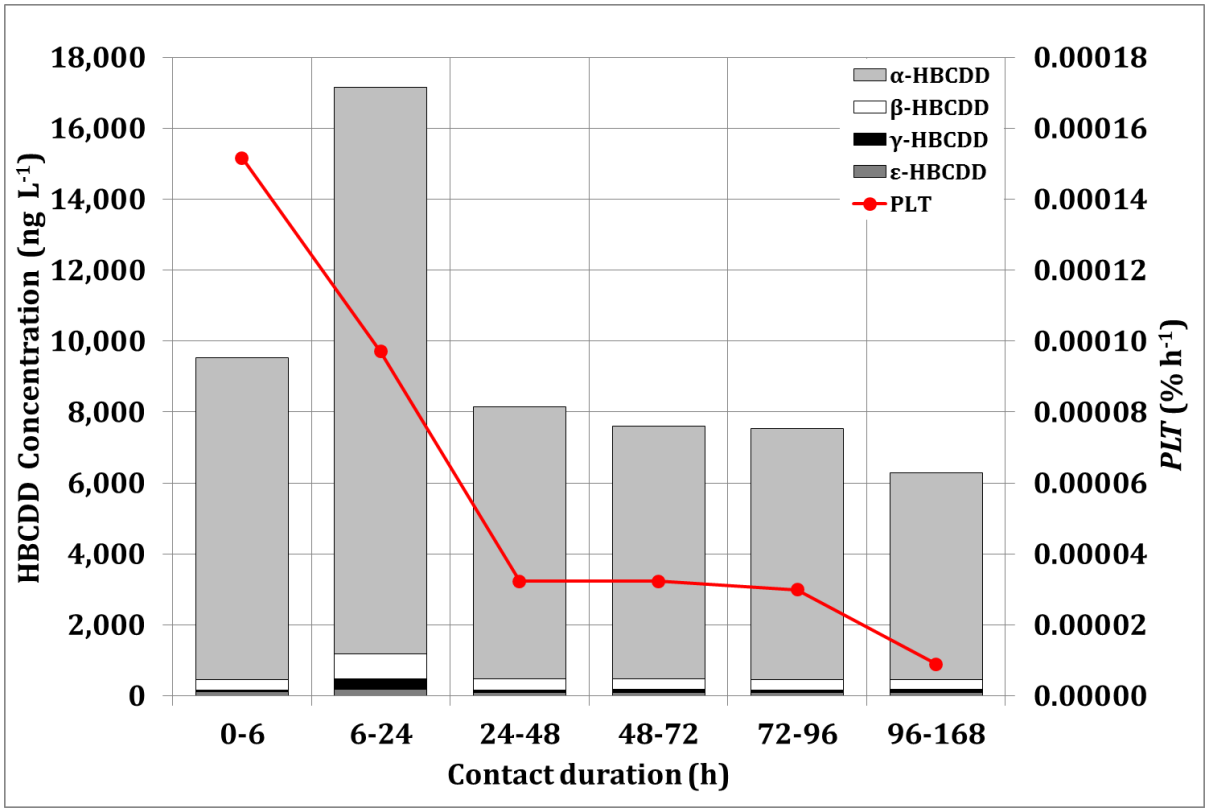
479



480

481 **Fig. 2 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate**
482 **produced during serial batch experiments on Textile A examining the effect of cyclical**
483 **wetting and draining.**

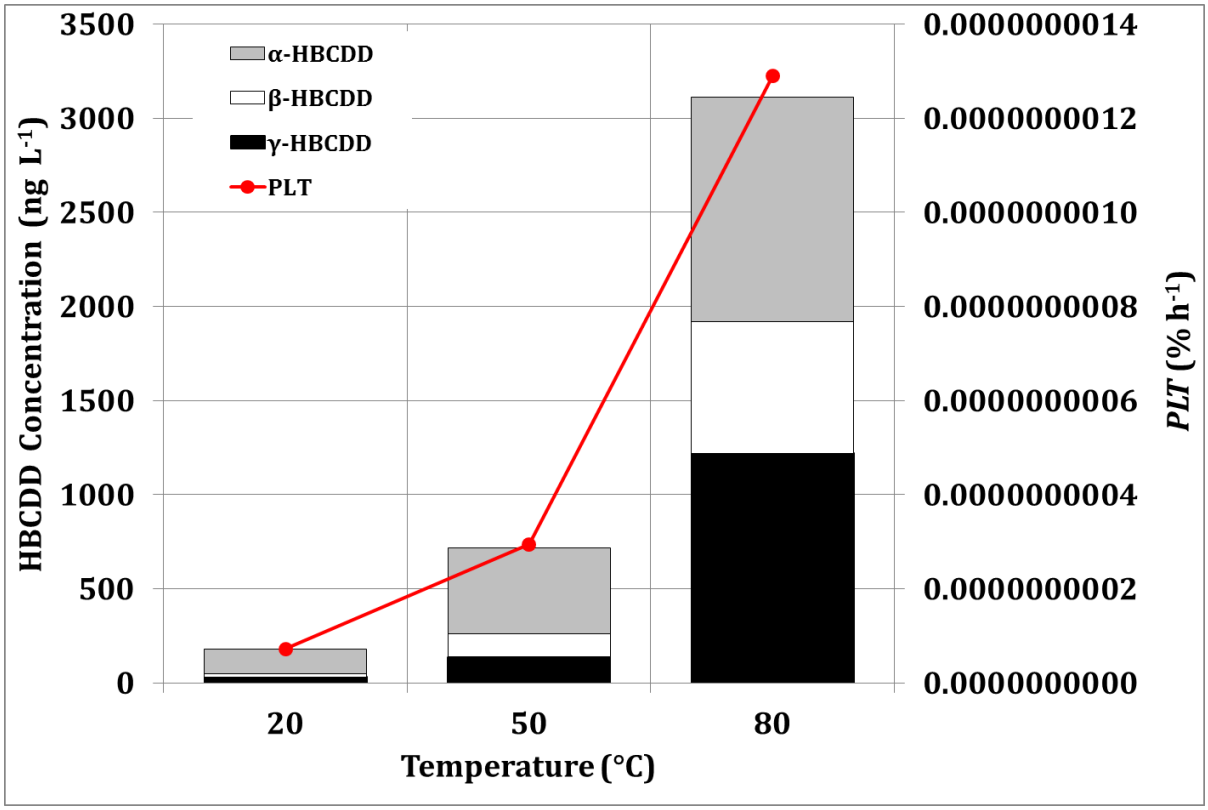
484



485

486 **Fig. 3 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate**
487 **produced during serial batch experiments on Textile B examining the effect of cyclical**
488 **wetting and draining.**

489



490

491 **Fig. 4 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) from Textile A at**
492 **different temperatures during 24h single batch experiments.**

493

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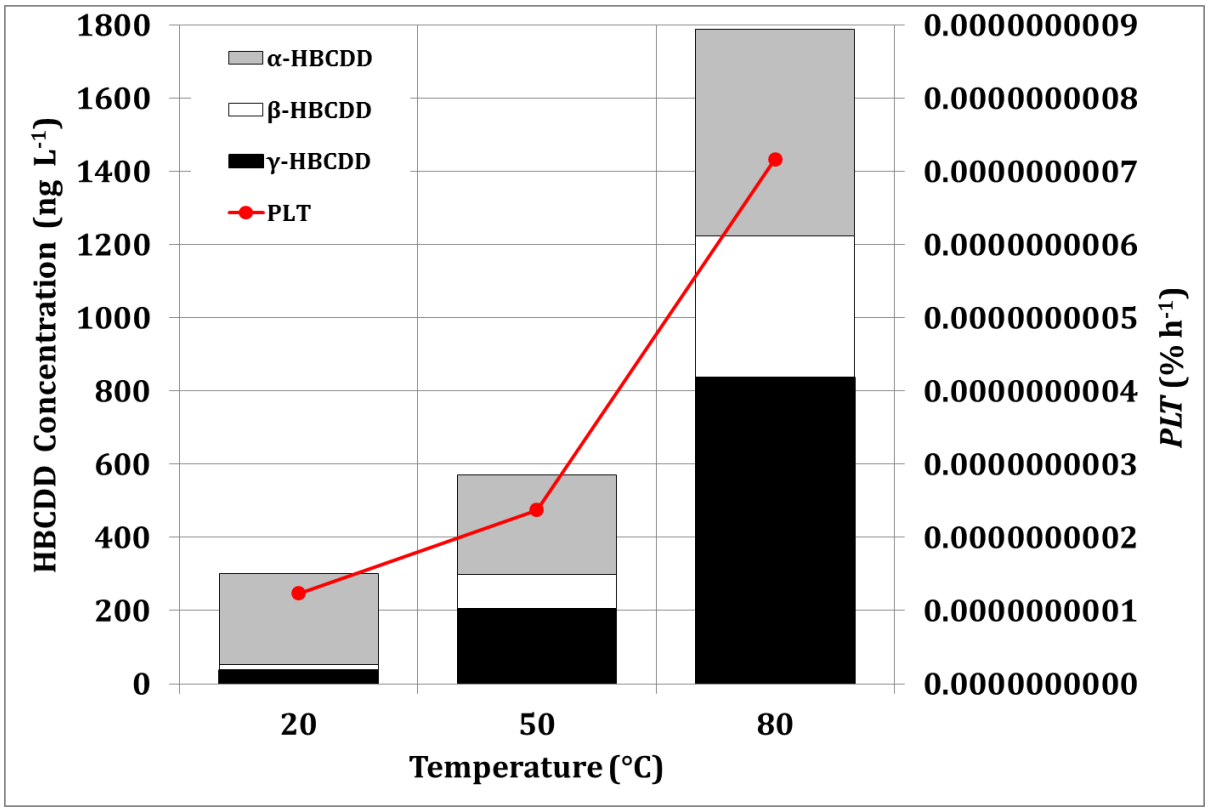


495

496 **Fig. 5 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) from Textile B at**
497 **different temperatures during 24h single batch experiments.**

498

1 **Table 1: Mean Concentrations (mg kg^{-1}) of HBCDDs in textiles used in this study**

Diastereomer/ Sample	α-HBCDD	β-HBCDD	γ-HBCDD	δ-HBCDD	ε-HBCDD	ΣHBCDD
Textile A	11,000 ± 55	4,500 ± 130	10,000 ± 160	<500	<300	26,000 ± 170
Textile B	9,900 ± 200	3,600 ± 100	10,000 ± 130	<500	<300	24,000 ± 420

Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

2

3

Table 2: Second order leaching rate constants (k) and saturated leaching capacities (C_s) obtained for HBCDD diastereomers for Textiles A and B[a]

Constant / Compound	Slope	y-intercept	C_s (ng L^{-1})	Observed max. conc. (ng L^{-1})	k (L ng^{-1} min^{-1})	*Two-tailed P value*	*Correlation coefficient: r*
Textile A							
β-HBCDD	0.0056	0.9249	180	220	0.000012	.000	0.945
γ-HBCDD	0.0043	1.1723	230	410	0.000007	.000	0.832
Textile B							
γ-HBCDD	0.0082	3.5252	120	380	0.000019	.000	0.896

[a]Data not shown for plots for which y-intercept and thus k values were negative.

Figure

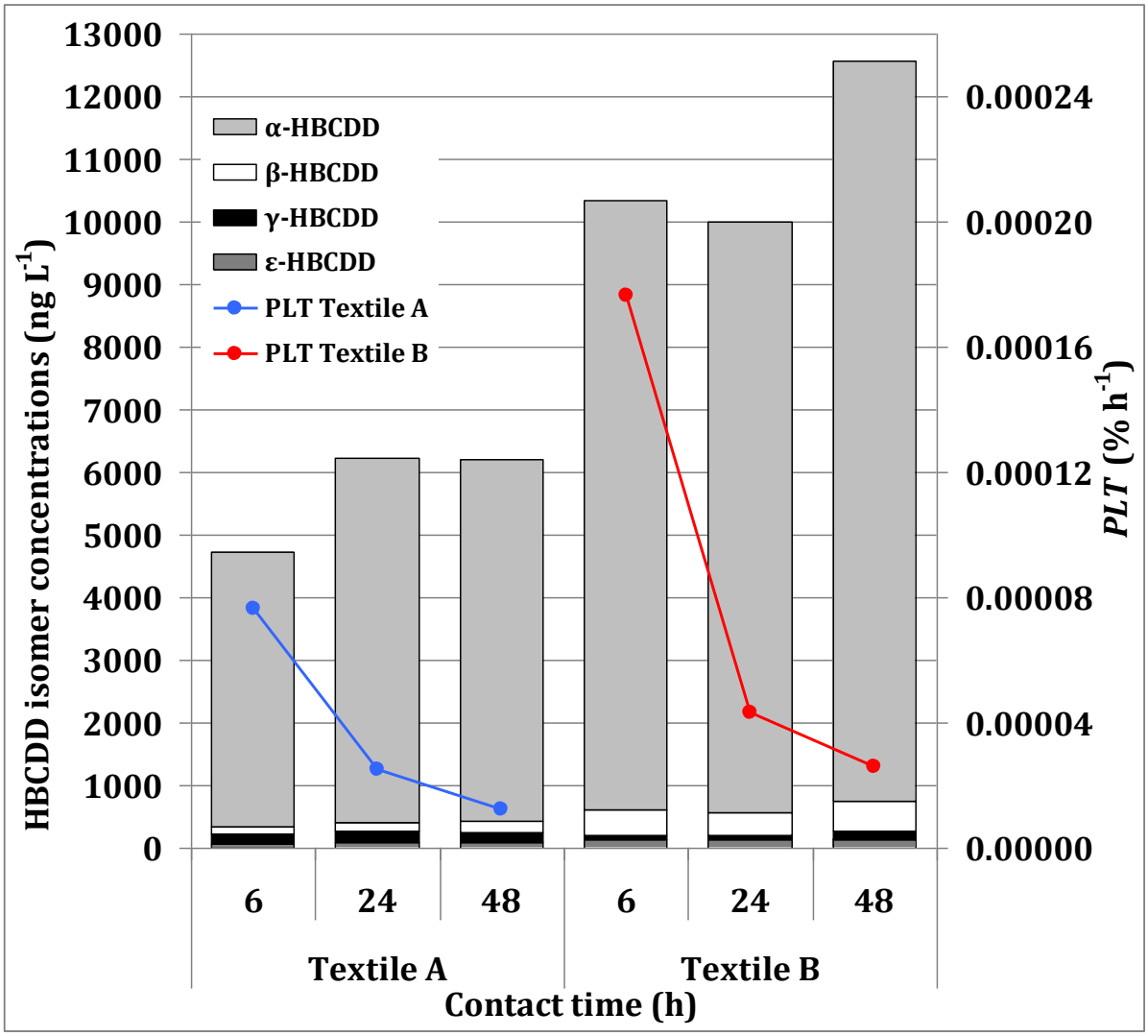


Fig. 1: Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate produced from single batch experiments on Textiles A & B for different agitation times.

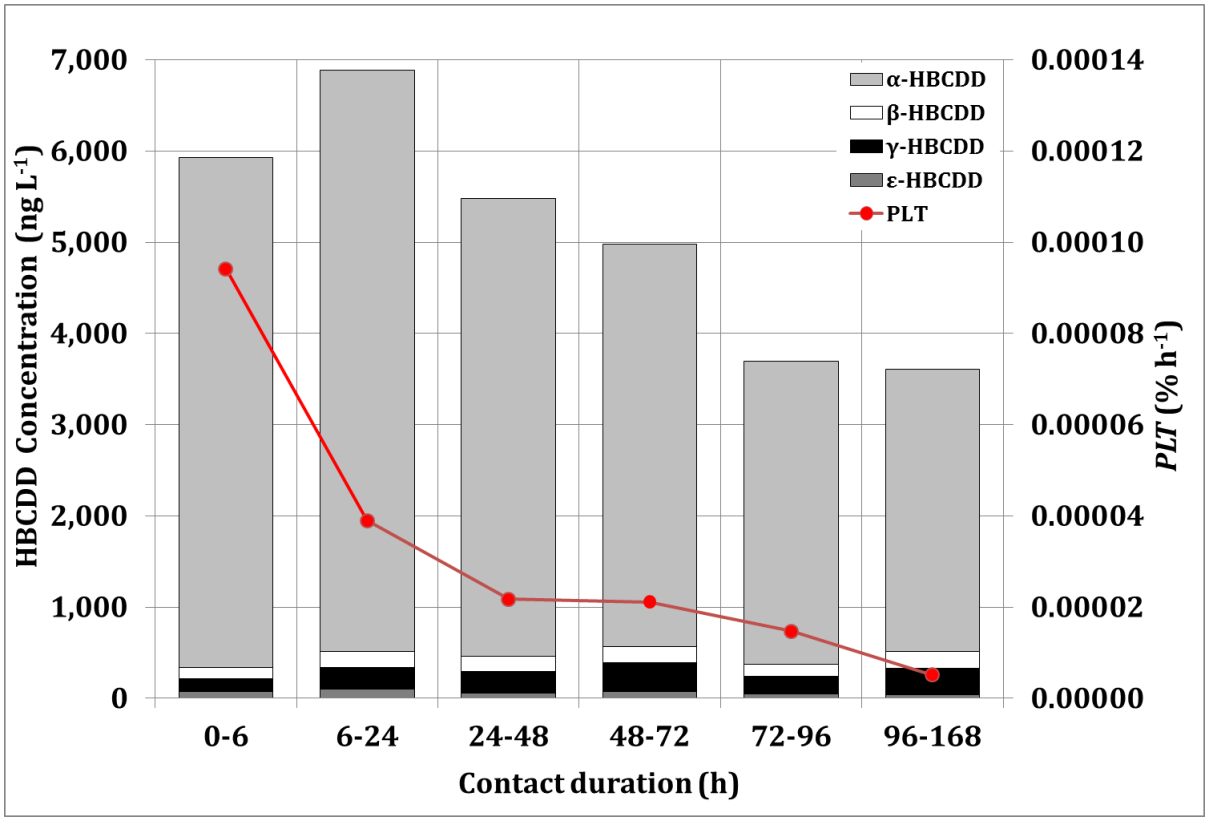


Fig. 2 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate produced during serial batch experiments on Textile A examining the effect of cyclical wetting and draining.

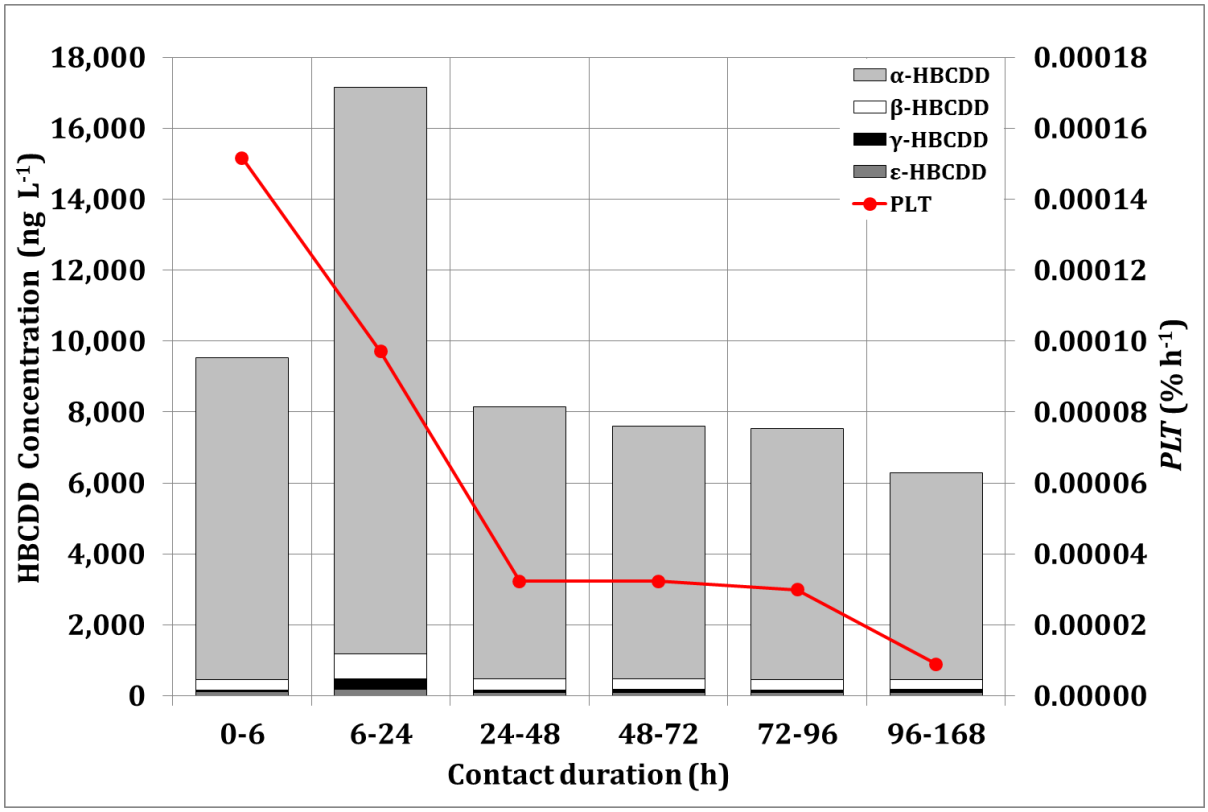


Fig. 3 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) in leachate produced during serial batch experiments on Textile B examining the effect of cyclical wetting and draining.

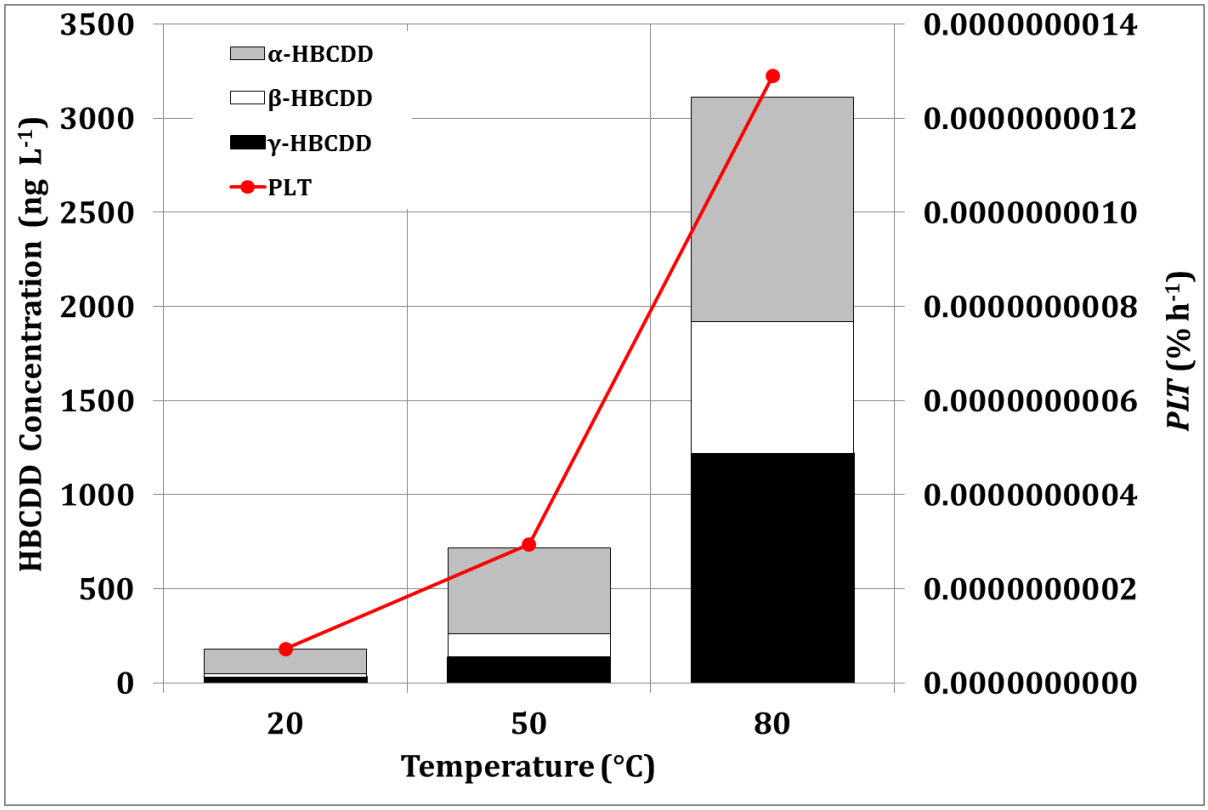
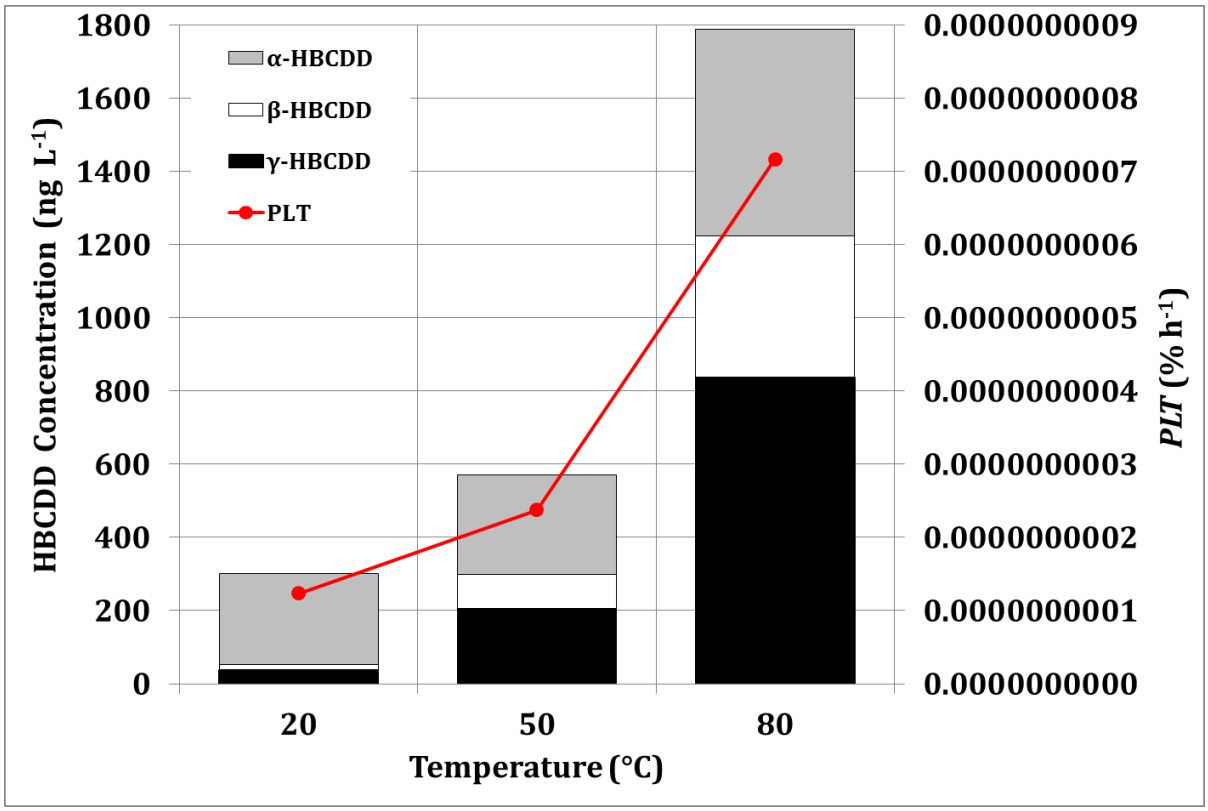


Fig. 4 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) from Textile A at different temperatures during 24h single batch experiments.

20



21

22 **Fig. 5 Mean (n=2) HBCDD concentrations (ng L^{-1}) and *PLT* values (% h^{-1}) from Textile B at**
23 **different temperatures during 24h single batch experiments.**

24

Supplementary Material

Click here to download Supplementary Material: Supplementary Information2.doc